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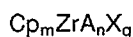
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(54) **Zirconium-based catalyst composition for polymerizing olefins.**

(57) An olefin polymerization catalyst composition comprising:

(1) a zirconium compound containing pi-bonded organic ligands and having the formula:

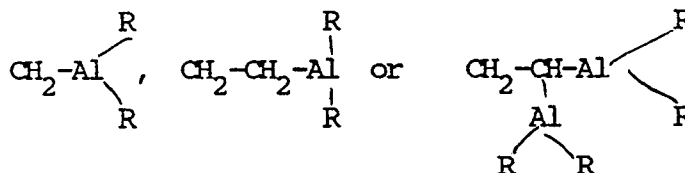


wherein:

Cp represents an unsubstituted or substituted cyclopentadienyl group,

m represents 1 or 2 or 3;

A represents a halogen or hydrogen atom or a C₁-C₆ alkyl group, a metalloalkyl group or a group of the formula:



wherein:

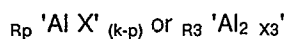
R represents a C₁ to C₁₀ alkyl group, a hydrogen, or halogen atom or a metalloalkyl group;

X represents a halogen or hydrogen atom or C₁ to C₆ alkyl group; n represents 0, 1 or 2; and q represents 0, 1 or 2;

providing that q + m + n is equal to the valence of zirconium; and

(2) a catalyst activator which comprises a mixture of

(i) an organoaluminum compound having the formula:



wherein:

R' represents a C₁ to C₆ alkyl group;

p represents 1 or 2;

X' represents a halogen atom; and

k represents the valence of aluminum; and

(ii) a dialkylmagnesium compound having the formula:



wherein:

R'' represents a C₂ to C₈ alkyl group;

R''' differs from R'' and represents a C₂ to C₈ alkyl group;

t represents the valence of magnesium; and

r represents 0.01 to 1.

ZIRCONIUM-BASED CATALYST COMPOSITION FOR POLYMERIZING OLEFINS AND POLYMERIZATION THEREWITH

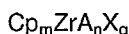
This invention relates to zirconium-based catalyst precursors activated with activators (also known as cocatalysts) comprising mixtures of two compounds; to the resulting catalyst compositions; and to the use thereof in processes for polymerizing and copolymerizing olefins, especially alpha-olefins.

It is known that certain zirconium complexes containing pi-bonded organic ligands, such as bis- (cyclopentadienyl) zirconium complexes, activated with an aluminum compound of the aluminoxane type, produce olefin polymers and copolymers, such as ethylene and propylene homopolymers, ethylene-butene and ethylene-hexene copolymers: U.S. 4,542,199 and U.S. 4,404,344. However, although such catalysts are very effective the aluminoxane cocatalysts are expensive and can be utilized efficiently only if Polymerization is effected in aromatic solvents. Accordingly, a need exists in the art for alternative activators for such zirconium-based catalysts.

The present invention seeks to provide a zirconium-based olefin polymerization catalyst composition comprising a zirconium-based catalyst comprising a zirconium-based catalyst precursor and an activator comprising a mixture of two compounds.

In accordance with one aspect of the present invention, there is provided an olefin polymerization catalyst composition comprising:

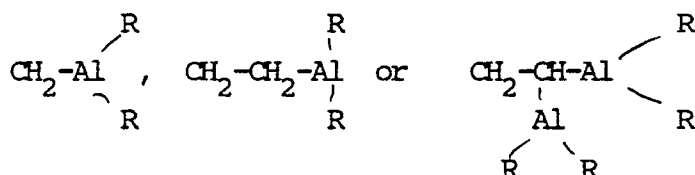
(1) a zirconium compound containing pi-bonded organic ligands and having the formula:



wherein:

Cp represents an unsubstituted or substituted cyclopentadienyl group,
m represents 1 or 2 or 3;

A represents a halogen or hydrogen atom or a C₁-C₆ alkyl group, a metalloalkyl group or a group of the formula:



wherein:

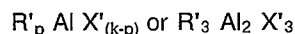
R represents a C₁ to C₁₀ alkyl group, a hydrogen, or halogen atom or a metalloalkyl group;

X represents a halogen or hydrogen atom or C₁ to C₆ alkyl group; n represents 0, 1 or 2; and q represents 0, 1 or 2;

providing that q + m + n is equal to the valence of zirconium; and

(2) a catalyst activator which comprises a mixture of

(i) an organoaluminum compound having the formula:



wherein:

R' represents a C₁ to C₆ alkyl group;

p represents 1 or 2;

X' represents a halogen atom; and

k represents the valence of aluminum; and

(ii) a dialkylmagnesium compound having the formula:



wherein:

R'' represents a C₂ to C₈ alkyl group;

R''' differs from R'' and represents a C₂ to C₈ alkyl group;
 t represents the valence of magnesium; and
 r represents 0.01 to 1.

The catalyst compositions of this invention polymerize olefins, such as alpha olefins, for example, ethylene, propylene, butene, hexene, or a mixture thereof, to homopolymers or copolymers having a density from 0.850 to 0.970 g/cc. The olefin polymerization reactions with this catalyst composition in both the aromatic and aliphatic hydrocarbon media.

In the zirconium compound, also known as a catalyst precursor, Cp is suitably an unsubstituted cyclopentadienyl group; m desirably represents 1 or 2, and preferably represents 2. The C₁-C₆ alkyl groups in the substituents A and X may be the same or different and are preferably straight chain normal alkyl groups, such as methyl, ethyl, n-propyl, n-butyl, n-pentyl or n-hexyl; the halogen atoms in the substituents A and X may be the same or different and include fluorine, chlorine, bromine or iodine; and suitable metalloalkyl groups in the substituents A and R may be the same or different and include Cp₂ Ti-CH₂ or Cp₂ Zr-CH₂-CH₂, where Cp is defined above. A is desirably a hydrogen or halogen atom, preferably a halogen atom, most preferably a chlorine atom; n preferably represents 2. Suitable substituents for Cp are C₁ to C₆ alkyl groups. Suitable zirconium compounds include bis (cyclopentadienyl) zirconium dihalide and bis (cyclopentadienyl) zirconium monoalkyl monohalide, wherein the halide is preferably a chlorine atom and the alkyl groups are C₁ to C₆ alkyl groups. Bis (cyclopentadienyl) zirconium dichloride is particularly preferred in one embodiment of the invention. Mixtures of the zirconium compounds may also be used.

The activator, also known as a catalyst promoter or cocatalyst, comprises a mixture of two compounds.

In the organoaluminum compound R' suitably represents a short-chain, C₁ to C₆ alkyl group, such as methyl, ethyl, n-propyl, n-hexyl or an isobutyl group, preferably a C₁ to C₃ alkyl group; X' represents a F, Br, Cl or I atom, preferably Br or Cl, and p is preferably 2. In one embodiment of the invention, diethylaluminum chloride, dimethylaluminum chloride and ethylaluminum sesquichloride are the preferred aluminum compounds. Mixtures of the organoaluminum compounds may also be used.

The preferred dialkylmagnesium compounds are those soluble in hydrocarbons, such as alkanes or aromatics, for example, heptane, hexane or toluene. In the dialkylmagnesium compound, R'' R''' are preferably C₂ to C₈ alkyl groups, such as ethyl, n-Propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl or n-octyl, especially methyl, ethyl, n-propyl or n-butyl, groups. Thus, suitable dialkylmagnesium compounds are n-butylethylmagnesium, butylpropylmagnesium, di-n-butylmagnesium, di-sec-butylmagnesium, n-butyl,sec-butylmagnesium, di-tert-butylmagnesium, di-n-hexylmagnesium, di-n-octylmagnesium, butyl,n-octylmagnesium. The most preferred dialkylmagnesium compound in one embodiment of the invention is n-butyl, sec-butylmagnesium (generally known as dibutylmagnesium). Mixtures of the dialkylmagnesium compounds may also be used.

The relative amounts of the organoaluminum compound to the dialkylmagnesium compound are not critical for the activation of the catalyst precursor but they may be critical to the polymerization activity of the activated catalyst composition. Thus, the relative amounts of the organoaluminum and the dialkylmagnesium compounds are such that the molar ratio of Al:Mg is from 0.1:1 to 10:1, preferably from 3:1 to 5:1. Conversely, the low molar ratios of Al:Mg, e.g., less than or equal to 1:1, produce catalyst compositions having relatively low activity. Neither the organoaluminum compounds nor the dialkylmagnesium compounds, if used separately, are capable of activating the zirconium compounds into active catalyst compositions.

The catalyst precursor is combined with the catalyst activator in a conventional manner, for example, by adding a solution of the precursor in a hydrocarbon solvent (such as a halogenated hydrocarbon or an aromatic solvent, for example, chloroform or toluene) to a solution of the activator in a hydrocarbon solvent.

Alternatively, a solution of one of the components of the activator (for example, the organoaluminum compound) in a solvent can be added to a solution of the precursor in a solvent, followed by the addition of the second component of the activator (the dialkyl magnesium compound) in a solvent.

The precursor may be activated in situ by adding the precursor and the mixture of the activators separately to the polymerization medium. The order of the mixing of the catalyst precursor and the activator components is not important. For example, the components of the activator can be mixed immediately prior to the introduction of the catalyst precursor, or, alternatively, the catalyst precursor and one of the components of the activator can be mixed first and the remaining component of the activator can be added later. It is also possible to combine both components of the activator before the introduction thereof into the polymerization medium, for example, for up to about 2 hours prior to the introduction thereof into the polymerization medium at a temperature from -40 to 100 °C.

Olefins, especially alpha-olefins, are polymerized with the catalysts prepared according to the present invention by any suitable process under conventional polymerization conditions, preferably in stirred

reactors under slurry conditions. The reaction under slurry conditions is carried out in a suitable liquid reaction medium, for example, an aromatic or an aliphatic hydrocarbon, such as toluene or hexane, respectively. The catalyst activity and the structure of the polymer products are influenced by the nature of the monomer or comonomers, the type of the reaction medium and by the Al:Mg molar ratio.

5 The linear polyethylene polymers prepared in accordance with the present invention are homopolymers of ethylene or copolymers of ethylene with one or more C₃ to C₁₀ alpha-olefins. Thus, copolymers having two monomeric units are possible as well as terpolymers having three monomeric units. Particular examples of such polymers include ethylene/propylene copolymers, ethylene/1-butene copolymers, ethylene/1-hexene copolymers, ethylene/1-octene copolymers, ethylene/4-methyl-1-pentene copolymers, ethylene/1-butene/1-
10 hexene terpolymers, ethylene/propylene/1-hexene terpolymers and ethylene/propylene/1-butene terpolymers. Ethylene/1-hexene is the most preferred copolymer polymerized in the process of and with the catalyst of this invention.

The linear low density polyethylene polymers produced in accordance with the present invention preferably contain at least about 80 percent by weight of ethylene units.

15 The following Examples illustrate the invention.

The properties of the polymers produced in the Examples and any calculated process parameters were determined by the following test methods:

Melt Index (MI), I₂: ASTM D-1238--Condition E--Measured at 190 C--reported as grams per 10 minutes.

High Load Melt Index (HLMI), I₂₁: ASTM D-1238--Condition F--Measured at 10.5 times the weight used
20 in the melt index test above.

Melting points of polymerization products were measured by the DSC (Differential Scanning Calorimetry) method. The sample heating rate of 2 °C/min was employed.

Copolymer compositions were measured by the infrared spectroscopic method, as described in the article of T. E. Nowlin, Y. V. Kissin and K. P. Wagner, HIGH ACTIVITY ZIEGLER-NATTA CATALYST FOR
25 THE PREPARATION OF ETHYLENE COPOLYMERS, published in 1988 in the Journal of Polymer Science:Part A:Polymer Chemistry, volume 26, pages 755-764.

EXAMPLE 1

30 (Ethylene Polymerization)

100 ml of anhydrous toluene was transferred under nitrogen into a stainless-steel, 0.5-liter reactor equipped with a magnetic stirrer. The catalyst components were added to the reactor in the following sequence: (a) 7.5 mmol of diethylaluminum chloride (introduced as a 25 weight % solution in hexane), after which the reactor was heated to 60 °C; (b) 0.006 mmol of bis(cyclopentadienyl)zirconium dichloride (as 1 g/l solution
35 in toluene); and (c) 2.0 mmol of dibutylmagnesium (as a 20 weight % solution in heptane). Ethylene was introduced into the reactor to maintain a total pressure of 180 psig. The polymerization reaction was carried out for 3 hours, and then the ethylene supply was stopped and the reactor allowed to cool. The reaction produced 10.6 g of linear, highly crystalline polyethylene with an I₂ of 3.0 g/10 min and a melting point of 134.2 °C.

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EXAMPLE 2

(Ethylene Polymerization)

The ethylene homopolymerization reaction was carried out in the same manner as that described in
45 Example 1, except for the amount of bis(cyclopentadienyl)zirconium dichloride used (0.0015 mmol). The polymerization reaction was carried out at 80 °C for 2 hours and produced 15.9 g of polyethylene with low molecular weight (I₂ = 107 g/10 min).

EXAMPLE 3

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(Ethylene/1-Hexene Copolymerization)

100 ml of anhydrous toluene and 20 ml of anhydrous 1-hexene was transferred under nitrogen into the 0.5-liter reactor. The catalyst components were added to the reactor in the following sequence: (a) 15.0 mmol of diethylaluminum chloride after which the reactor was heated to 60 °C; (b) 0.009 mmol of bis-
55 (cyclopentadienyl)zirconium dichloride; and (c) 4.0 mmol of dibutylmagnesium. Ethylene was introduced into the reactor to maintain a total pressure of 180 psig. The copolymerization reaction was carried out for 3 hours and produced 22.5 g of ethylene/1-hexene copolymer with a I₂ of 31 g/10 min. The copolymer contained 5.2 weight % of 1-hexene and had a melting point of 126.8 °C.

EXAMPLE 4(Ethylene/1-Hexene Copolymerization)

100 ml of anhydrous toluene and 40 ml of anhydrous 1-hexene was transferred under nitrogen into the 0.5-liter reactor. The catalyst components were added to the reactor in the following sequence: (a) 1.5 mmol of diethylaluminum chloride; (b) 0.8 mmol of dibutylmagnesium, after which the reactor was heated to 60 °C; and (c) 0.0041 g (0.0123 mol) of solid bis(cyclopentadienyl) zirconium dichloride. Ethylene was introduced into the reactor to maintain the total pressure of 120 psig. The copolymerization reaction was carried out for 2 hours and produced 52.0 g of ethylene/1-hexene copolymer with a I_2 of 228. The copolymer contained 12.4 weight % of 1-hexene and had a melting point of 115.3 °C.

EXAMPLE 5(Ethylene/1-Hexene Copolymerization)

100 ml of anhydrous toluene and 40 ml of anhydrous 1-hexene was transferred under nitrogen into the 0.5-liter reactor. The catalyst components were added to the reactor in the following sequence: (a) 7.5 mmol of dimethylaluminum chloride (as a 25 weight % solution in heptane); (b) 2.0 mmol of dibutylmagnesium, after which the reactor was heated to 80 °C; (c) 0.006 of bis(cyclopentadienyl)zirconium dichloride in toluene solution. Ethylene was introduced into the reactor to maintain the total pressure of 180 psig. The copolymerization reaction was carried out for 1 hour and produced 23.1 g of low molecular weight ethylene/1-hexene copolymer with a I_2 of 900 g/10 min and a melting point of 122.5 °C.

EXAMPLE 6(Ethylene/1-Hexene Copolymerization)

200 ml of anhydrous n-hexane and 50 ml of anhydrous 1-hexene was transferred under nitrogen into the 0.5-liter reactor. The catalyst components were added to the reactor in the following sequence: (a) 7.5 mmol of diethylaluminum chloride; (b) 2.0 mmol of dibutylmagnesium, after which the reactor was heated to 80 °C; (c) 0.009 mmol of bis(cyclopentadienyl)zirconium dichloride in toluene solution. Ethylene was introduced into the reactor to maintain the total pressure of 150 psig. The copolymerization reaction was carried out for 2 hours and produced 22.2 g of ethylene/1-hexene copolymer with a I_{21} of 11.1. The copolymer contained 10.6 weight % of 1-hexene and had a melting point of 125.2 °C.

EXAMPLE 7(Ethylene/1-Hexene Copolymerization)

200 ml of anhydrous n-hexane and 50 ml of anhydrous 1-hexene was transferred under nitrogen into the 0.5-liter reactor. The catalyst components were added to the reactor in the following sequence: (a) 7.5 mmol of diethylaluminum chloride; (b) 2.0 mmol of dibutylmagnesium, after which the reactor was heated to 80 °C; (c) 0.009 mmol of bis(cyclopentadienyl)zirconium dichloride in toluene solution. Reactor was pressurized with 6 psia of hydrogen to control the molecular weight. Ethylene was introduced into the reactor to maintain the total pressure of 150 psig. The copolymerization reaction was carried out for 2 hours and produced 26.9 g of ethylene/1-hexene copolymer with a I_2 of 0.61 and a melting point of 125.7 °C.

EXAMPLE 8(Ethylene/1-Hexene Copolymerization)

200 ml of anhydrous n-hexane and 50 ml of anhydrous 1-hexene was transferred under nitrogen into the 0.5-liter reactor. The catalyst components were added to the reactor in the following sequence: (a) 7.5 mmol of dimethylaluminum chloride; (b) 2.0 mmol of dibutylmagnesium, after which the reactor was heated to 80 °C; (c) 0.009 mmol of bis(cyclopentadienyl)zirconium dichloride in toluene solution. Ethylene was introduced into the reactor to maintain the total pressure of 180 psig. The copolymerization reaction was carried out for 2 hours and produced 26.2 g of ethylene/1-hexene copolymer with a I_2 of 1.1. The copolymer contained 3.2 weight % of 1-hexene and had a melting point of 127.8 °C.

EXAMPLE 9(Ethylene/1-Hexene Copolymerization)

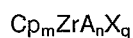
100 ml of anhydrous toluene and 40 ml of anhydrous 1-hexene was transferred under nitrogen into the 0.5-liter reactor. The catalyst components were added to the reactor in the following sequence: (a) 4.5 mmol of diethylaluminum fluoride (introduced as a 25 weight % solution in heptane); (b) 0.006 mmol of bis-(cyclopentadienyl)zirconium dichloride (as 1 g/l solution in toluene); (c) 1.0 mmol of dibutylmagnesium (as a 20 weight % solution in heptane). Ethylene was introduced into the reactor in a sufficient amount to maintain the total pressure of 180 psig.

The copolymerization reaction was carried out for 2 hours and produced 15.6 g of ethylene/1-hexene copolymer. The copolymer contained 2.4 weight % of 1-hexene copolymer. The copolymer contained 2.4 weight % of 1-hexene and had the I_2 value of 0.74 g/10 min; its melting point was 118.6 °C.

Claims

1. An olefin polymerization catalyst composition comprising:

(1) a zirconium compound containing pi-bonded organic ligands and having the formula:

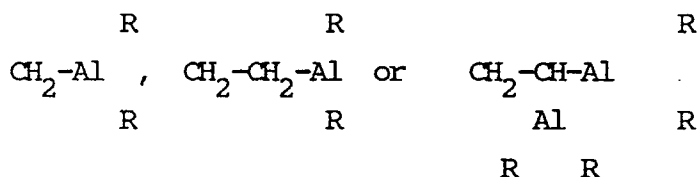


wherein:

Cp represents an unsubstituted or substituted cyclopentadienyl group,

m represents 1 or 2 or 3;

A represents a halogen or hydrogen atom or a C_1 - C_6 alkyl group, a metalloalkyl group or a group of the formula:



wherein:

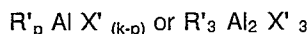
R represents a C_1 to C_{10} alkyl group, a hydrogen, or halogen atom or a metalloalkyl group;

X represents a halogen or hydrogen atom or C_1 to C_6 alkyl group; n represents 0, 1 or 2; and q represents 0, 1 or 2;

providing that $q + m + n$ is equal to the valence of zirconium; and

(2) a catalyst activator which comprises a mixture of

(i) an organoaluminum compound having the formula:



wherein:

R' represents a C_1 to C_6 alkyl group;

p represents 1 or 2;

X' represents a halogen atom; and

k represents the valence of aluminum; and

(ii) a dialkylmagnesium compound having the formula:



wherein:

R'' represents a C_2 to C_8 alkyl group;

R''' differs from R'' and represents a C_2 to C_8 alkyl group;

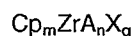
t represents the valence of magnesium; and

r represents 0.01 to 1.

2. A catalyst according to claim 1 wherein m represents 1 or 2, A represents a hydrogen or halogen atom

and n is 2.

3. A catalyst according to claim 1 or 2 wherein, in the organoaluminum compound, R represents a C₁ to C₃ alkyl group, X' represents a F, Br, Cl or I atom, and p is 2.
4. A catalyst according to claim 3 wherein the organoaluminum compound comprises diethylaluminum chloride, dimethylaluminum chloride or ethylaluminum sesquichloride.
5. A catalyst according to any preceding claim wherein, in the dialkyl magnesium compound, R'' and R''' represent an ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl or n-octyl group.
6. A catalyst according to claim 5 wherein the dialkyl magnesium compound is n-butyl, sec-butylmagnesium.
7. A catalyst according to claim 6 wherein the amounts of the aluminum and magnesium compounds are such that the Al:Mg molar ratio is 0.1:1 to 10:1.
8. A process for polymerizing at least one olefin comprising contacting the olefin under olefin polymerization conditions with a catalyst composition comprising:
 - (1) a zirconium compound containing pi-bonded organic ligands and having the formula:

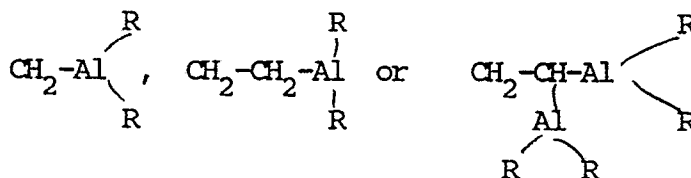


wherein:

Cp represents an unsubstituted or substituted cyclopentadienyl group;

m represents 1, 2 or 3;

A represents a halogen or hydrogen atom or a C₁ to C₆ alkyl group, a metalloalkyl group or a group of the formula:



wherein:

R represents a C₁ to C₁₀ alkyl group, a hydrogen or halogen atom or a metalloalkyl group;

X represents a halogen or hydrogen atom or a C₁ to C₆ alkyl group;

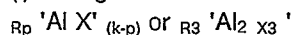
n represents 0, 1 or 2; and

q represents 0, 1 or 2;

providing that q + m + n is equal to the valence of zirconium; and

(2) a catalyst activator which comprises a mixture of

(i) an organoaluminum compound having the formula:



wherein:

R represents a C₁ to C₆ alkyl group;

p represents 1 or 2;

X' represents a halogen atom; and

k represents the valence of aluminum; and

(ii) a dialkylmagnesium compound having the formula:



wherein:

R'' represents a C₂ to C₈ alkyl group;

R''' differs from R'' and represents a C₂ to C₈ alkyl group;

t represents the valence of magnesium; and
r represents 0.01 to 1.

9. A process according to claim 8 wherein the alpha-olefin feed is a mixture of ethylene and at least one C₃ to C₁₀ alpha-olefin.

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